

Determination of Atmospheric
Phosphorus Addition to Lake Michigan

Wisconsin Univ.-Milwaukee

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TO LAKE MICHIGAN

by

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FOREWORD

The accelerated rate of eutrophication, or aging, of the Great Lakes is a topic that has been the object of extensive research and study. Increased concentrations of phosphorus in the lakes have been identified as making a major contribution to this undesirable process. It is necessary to have an understanding of the modes of interaction between the lake ecosystems and phosphorus to determine more intelligently the required steps to minimize man's impact on this valuable resources.

This report presents the results of a detailed study to determine the amount of phosphorus entering Lake Michigan from atmospheric sources. Seasonal as well as variations in geographical deposition rates are determined.

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ABSTRACT

Bulk precipitation was collected on a monthly basis in the Lake Michigan basin for 18 months during 1975-1976 to determine atmospheric P loadings to Lake Michigan. The sampling network consisted of bulk collectors at 23 land stations and 2 in-lake buoys located off urban and rural areas. Annual TP loading to Lake Michigan for 1976 based on loading rates of 0.184 and 0.303 $\mu\text{g}/\text{cm}^2/\text{mo}$ for the north and south basins, respectively was 1.69×10^6 Kg/year, representing $\sim 16\%$ of the total P budget. North and south basins showed different TP loading properties with $\sim 62\%$ depositing in the south basin. Seasonal variations in loading rates showed maxima in late spring and early summer, and minima in winter. In-lake buoy samplers yielded enhanced loading of TP compared to land stations. Wet-only precipitation concentrations for TP averaged 15% of bulk deposition values. Weighted-average TP concentrations in bulk precipitation were 0.050 and 0.064 mg/l in the north and south basins, respectively. Atmospheric TP loading was closely correlated to Ca and Mg loading, independent of precipitation amount, and exhibited a large dry fall component. Wind-blown soil and re-entrained dust are believed to be the major sources of atmospheric phosphorus addition to Lake Michigan.

Annual loadings (1976) of various chemical components to Lake Michigan in units of 10^6 Kg are:

TP, 1.69; TOC, 153.5; Si 7.99; SO_4 , 135.4; Cl, 82.5; Ca, 103.4; Mg, 22.5; Na, 16.2; K, 9.60; particulates, 818.5.

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SECTION 1

INTRODUCTION

Considerable effort has been expended in recent years investigating the sources and cycling of potential limiting nutrients (P, N, C) in marine and freshwater environments. However, only recently have atmospheric inputs of nutrients, especially phosphorus (P) and nitrogen (N) been considered as important sources to small and large lake systems. Most effort and funding have concentrated on restricting nutrient inputs from point sources such as industrial and municipal discharges. Lakes Michigan and Superior have large surface areas, but small drainage basins suggesting the atmosphere may be a significant source of natural and anthropogenic components representing a sizeable portion of the total nutrient budget.

Recent studies by Canada Centre for Inland Waters (1975), Murphy (1974), Murphy and Doskey (1976), Shiomi and Kuntz (1973), Casey and Salbach (1974) and IJC (1976) indicate clearly that atmospheric P inputs to the Great Lakes may represent a sizeable portion of the overall nutrient budget. Murphy and Doskey (1976) using event, wet-only precipitation data at six sites estimated the atmospheric loading of P to Lake Michigan as 1×10^6 Kg/year, which represented about 18% of the 1974 P budget of the lake. Approximately 40% of the atmospheric P was in the "dissolved reactive" form and 0.6×10^6 Kg/year was in a form which could be mobilized by aquatic organisms.

Casey and Salbach (1974) calculated the atmospheric P input to Lake Ontario to be 1.7×10^6 Kg/year representing ~ 10% of the total P budget. Similar studies on the Upper Great Lakes (IJC, 1976) found that ~ 12.1% and 19.3% of the total P budget of Lakes Huron and Superior, respectively, were derived from the atmosphere.

Enhanced loading of major chemical parameters and nutrients to Lake Michigan on an historical basis has resulted in a steady increase in lake water concentrations of P (Vaughn and Reed, 1974), SO_4 , Cl, Na, K and total dissolved solids (Beeton, 1965, 1969). Schelske and Stoermer (1971) contend that accelerated eutrophication of Lake Michigan stimulated by phosphorus inputs has resulted in an increased rate of silica depletion by diatoms in the surface waters during summer stagnation leading to undesirable changes in biological species' diversity. As P from point sources decrease as a result of treatment advances, other P sources become more important.

The objective of this investigation was to determine the atmospheric contribution of P to the nutrient budget of Lake Michigan and to delineate possible sources and atmospheric removal mechanisms.

SECTION 2

CONCLUSIONS

Annual P (TP) loading to Lake Michigan from atmospheric sources was 1.69×10^6 Kg based on loading rates of 0.184 and 0.303 $\mu\text{g}/\text{cm}^2/\text{mo}$ for the north and south basins, respectively in 1976. This represents 15.7% of the total P budget based on 1975 data.

In 1976, atmospheric deposition of TP in Lake Michigan was dominated by a dry fall component likely derived from wind-blown soil. Actual in-lake loading of TP may exceed loading calculated from land-based stations by up to 50%.

The weighted-average concentration of TP in bulk precipitation was 0.050 and 0.064 mg P/l in the north and south basins, respectively, as compared to the average lake water concentration of 0.01 mg P/l. Only 5-6% of the P collected in urban areas and 18 to 38% of the P collected in rural areas on a monthly basis was "dissolved inorganic P".

Loadings of all chemical parameters measured were greater in the southern compared to the northern basin. Atmospheric loading of P and other chemicals was generally greatest in spring and summer and minimum in winter.

Atmospheric P inputs were closely correlated with soil-derived components. Atmospheric loading of TOC and SO_4 exhibited evidence of regional transport and deposition.

The pH of wet-only precipitation averaged one pH unit lower than bulk deposition.

SECTION 3

RECOMMENDATIONS

That phosphorus be included as an air quality parameter and criteria established.

That the relationship of land use to atmospheric phosphorus addition to the Great Lakes be determined.

That phosphorus concentrations in rainfall, dry fallout and aerosol particles over Lake Michigan be determined.

That sampling for Total Organic Carbon (TOC), Calcium (Ca), Chloride (Cl), Sulfate (SO_4) and pH be included in the air quality monitoring program for the Great Lakes.

SECTION 4

EXPERIMENTAL PROCEDURES

DESCRIPTION OF STUDY AREA

The precipitation collection network for determination of the atmospheric P addition to Lake Michigan comprised the Lake Michigan basin and two sites in the northern half of the lake which are land-locked and served as remote stations. Precipitation stations were located in the states of Wisconsin, Illinois, Indiana and Michigan. The largest fraction of the land component in the basin is contributed by Wisconsin and Michigan which also provide the greatest tributary inputs from the Grand and St. Joseph Rivers (Michigan) and the Fox and Menominee-Milwaukee Rivers (Wisconsin). Illinois and Indiana in the Chicago-Gary area contribute negligible surface flow to the lake, but represent major sources of atmospheric input as a result of intense urban and industrial activity (Winchester and Nifong, 1971).

Lake Michigan has a surface area of 5.80×10^4 Km² as compared to a drainage basin of 1.178×10^5 Km² and lies wholly within the boundary of the contiguous United States. Average depth and volume of Lake Michigan are 84m and 4.87×10^3 Km³, respectively (Mortimer, 1976). Average annual precipitation is 78.7 cm (Schelske and Roth, 1973).

Figure 1 depicts the 23 precipitation collection sites for the determination of atmospheric P addition to Lake Michigan and Table I depicts their location. The precipitation network was designed to collect bulk precipitation (wet and dry fall) representative of rural, municipal and industrial regions of the basin adjacent to the lake so that atmospheric loading could be derived. Urban and industrial contributions to atmospheric inputs were investigated with a heavy density of collection sites in the Milwaukee, Wisconsin and Chicago, Illinois-Gary, Indiana metropolitan centers. Loading values from these areas represent averages of monthly-collected precipitation samples for sites 7, 9 and 10 (Milwaukee) and 12 through 15 (Chicago). Average loading values were derived for intensely sampled areas so as not to bias regional atmospheric inputs.

Sampling sites in the northern half of the lake represent rural and regional inputs while collection sites in the southern half are more closely related to urban and industrial sources. The northern and southern basins were defined as one-half of the total lake surface area which parallels closely geographical distributions. Sampling sites expected to be more representative of actual in-lake precipitation were located at Beaver Island, Michigan (#18) and two in-lake buoys located off the western shore opposite the Milwaukee metropolitan area (#10B) and Kohler-Andre State Park (#6B). The buoys were moored in ~ 23 m of water ~ 3-6 Km offshore.



Figure 1. Location of Lake Michigan Precipitation Stations.

TABLE 1.
ATMOSPHERIC SAMPLING SITE LOCATIONS

Site Number	Name	Location
1	Watersmeet, Mich.	45° 17' N, 89° 07' W
2	Stevens Point, Wisc.	44° 31.6' N, 89° 34' W
3	Green Bay, Wisc.	44° 30' N, 88° 05' W
4	Sister Bay, Wisc.	45° 09' N, 87° 04' W
5	Kewaunee, Wisc.	44° 17' N, 87° 32.5' W
6	Sheboygan, Wisc.	43° 39' N, 87° 44' W
7	Milwaukee, Wisc.	43° 04.5' N, 87° 51' W
8	Milwaukee, Wisc.	43° 02' N, 87° 50' W
9	Milwaukee, Wisc.	42° 57' N, 87° 54' W
10	Cudahy, Wisc.	42° 57' N, 87° 48' W
11	Zion, Ill.	42° 25.5' N, 87° 48' W
12	Wilmette, Ill.	42° 04.6' N, 87° 41' W
13	Chicago, Ill.	41° 52' N, 87° 36.9' W
14	Chicago, Ill.	41° 55.3' N, 87° 39' W
15	Calumet, Ill.	41° 43' N, 87° 31' W
16	Indiana Dunes	41° 49.8' N, 87° 04' W
17	Ludington, Mich.	43° 57' N, 86° 25.5' W
18	Beaver Island, Mich.	45° 44.8' N, 85° 30.5' W
19	Douglas Lake, Mich.	45° 55' N, 84° 68' W
20	Hammond Bay, Mich.	45° 30' N, 84° 02' W
21	Sleeping Bear Sand Dunes	44° 72.3' N, 86° 01.8' W
22	Grand Haven, Mich (Mich)	43° 03.8' N, 86° 14.8' W
23	St. Joseph, Mich.	42° 05.3' N, 86° 29.5' W

Bulk-precipitation collectors were deployed in the field 1-4 July, 1975 and operated through 31 December, 1976. In-lake buoy collectors were operational for three months from August through October, 1976. Twenty-three sites were equipped with bulk collectors of which 19 were monitored for the entire study period. Two stations, Watersmeet, Michigan (#1) and Stevens Point, Wisconsin (#2) were used to compare loading rates distant from Lake Michigan. Two Atomic Energy Commission (AEC) wet-only samplers (Galloway, 1976) were deployed at sites #5 and #8 to obtain an estimate of the dry fall component. Except for only a few samplers, all precipitation was collected at sites within 0.5 Km of Lake Michigan in areas which would receive minimal influence from local sources.

DESCRIPTION OF SAMPLING SITES

A brief description of each sampling site follows:

Site #1 consisted of a bulk collector located on the lawn of the Ottawa National Forest headquarters in Watersmeet, Michigan. Entrance to the building and collector was via a base gravel road.

A second bulk collector (#2) was located on the roof of the Science Center of the University of Wisconsin-Stevens Point approximately 15 meters above ground level. Stevens Point has a population of 23,471 and possesses paper mill and light manufacturing capabilities.

A third bulk collector (#3) was located at the meteorological field of the University of Wisconsin-Green Bay. Several weather monitoring devices were enclosed within a fenced area of the university grounds about 1 Km east of Green Bay and Lake Michigan. Green Bay (population 87,809) has light and heavy manufacturing including several of the largest paper companies in the United States.

A fourth bulk collector (#4) was located on a private lawn near Sister Bay, Wisconsin adjacent to an agricultural area about 2 Km from Lake Michigan.

The fifth bulk collector (#5) and one AEC wet-only sampler was located on the roof of the Point Beach Nuclear Power Plant visitor's center about 4 m above street level and 0.1 Km from Lake Michigan. Agriculture, commercial fishing and tourism represent the major activities of nearby Kewaunee (population 2,901) and Two Rivers, Wisconsin (population 13,732).

The sixth bulk collector (#6) was located on the beach of Kohler-Andre State Park about 3.5 Km north of Sheboygan, Wisconsin (population 48,484). The area is bordered by scotch pine (*Pinus strobus*) with agriculture predominant inland. A buoy tower and bulk collector (#6B) was located 3.2 Km east of the beach in about 23 m of water from 2 August, 1976 to 3 November, 1976.

Bulk collectors 7, 8, 9 and 10 were located in the Milwaukee metropolitan area (population 717,372) on the south lawn of the Linwood Avenue Water Filtration Plant on the roof of the University of Wisconsin Great Lakes Research Facility. On the lawn of the U.S. Weather Service at Billy Mitchell

Field-International Airport and on the roof of the Cudahy, Wisconsin Senior High School. Most bulk collectors were within 0.5 Km of Lake Michigan. Precipitation data at site #8 (GLRF) was influenced by a local coke plant and foundry 0.5 Km to the west and was not used to calculate loading values to Lake Michigan. An AEC wet-only sampler was deployed at site #8 and operated from April-December, 1976 to investigate wet-only deposition in an urban area. The second buoy tower and bulk collector was located 6.4 Km east of Milwaukee opposite site #10 and operated from 2 August-3 November, 1976.

Bulk collector #11 was located at Illinois Beach State Park, Zion, Illinois approximately 4 m above ground level and 50 m from Lake Michigan. Light industry and the nuclear power plant at Zion are in the area. The park is heavily wooded with a deciduous flora.

Bulk collector #12 was located on the lawn of the U.S. Coast Guard Station at Wilmette Harbor north of Chicago about 50 m from Lake Michigan.

Bulk collectors were located at sites 13, 14 and 15 in the Chicago area on the roof of the John G. Shedd Aquarium, on the roof of the science building at DePaul University and on the lawn of the U.S. Coast Guard Station at Calumet Harbor near the Indiana-Illinois border, respectively. The collector at DePaul University was located about 2 Km from Lake Michigan, but #13 and #15 were within 0.5 Km of the lake. Site #15 was influenced by nearby steel manufacturing while #14 reflected urban activity.

Bulk collector #16 was located on the beach pavillion roof at Indiana Dune State Park. Large sand dunes and beach succession flora compose the surrounding area.

Bulk collector #17 was located on the lawn of the Biological Station of the U.S. Bureau of Sport Fisheries in Ludington, Michigan about 5 Km from the lake.

Bulk collector #18 was located on Beaver Island (area of 140 Km²) in the northern reaches of Lake Michigan adjacent to a similar collector maintained by the Michigan Department of Natural Resources. Local activity consists of tourism, commercial fishing and some agriculture.

Bulk collectors #19 and #20 were located at the Douglas Lake Biological Station of the University of Michigan and Hammond Bay Biological Station of the U.S. Bureau of Sport Fisheries, respectively, from July-November, 1975. Sampling at these locations terminated in November 1975.

Bulk collectors 21, 22 and 23 were operated throughout 1976 at Sleeping Bear Sand Dunes National Lakeshore near the mouth of the Grand River at Grand Haven State Park and on the roof of St. Joseph High School, St. Joseph, Michigan, respectively. Most of the bulk collectors were located within 0.5 Km of Lake Michigan. The combined population of the St. Joseph-Benton Harbor, Michigan area is 27,523.

Precipitation Sampling

Precipitation was collected primarily with bulk collectors (wet and dry fall) based at either 23 land-based stations or two in-lake buoys. Bulk precipitation data was augmented with limited amounts of wet-only collected samples. The bulk collector was similar to that used by Kramer (CCIW, 1975) and consisted of a central collection standpipe (25 cm diameter, 506.45 cm² surface area) surrounded by an Alter windshield and a bird-off to limit sample contamination. The standpipe collector was designed originally as a snow sampler which also operates effectively as a rain sampler with some modification. The sampler is similar to that used previously in determining atmospheric inputs of chemical components to Lakes Superior and Huron (IJC, 1976). The bulk collector has been evaluated by Berry (1975) and Galloway (1976) for use in collecting rain and dry fallout for chemical analysis. Rawls *et al.*, (1975) compared the rainfall collection efficiency of standpipe-type samplers with a modified Alter windshield and a rigid Alter windshield. The windshields did not produce variable collection efficiency on the average, and either model can be used to compute actual precipitation.

Bulk precipitation was collected in an inner liner made of 4-mil thickness polyethylene. In the summer of 1975, a 2 mm, Nyltex Nylon screen was placed in the liner to limit introduction of coarse debris and large insects. In 1976, a 0.5 mm screen replaced the 2 mm screen. In addition, a polyethylene funnel was placed at 0.3 m above the bottom of the liner and the liner restricted by tying at the funnel outlet to limit evaporation. Summer evaporative losses with the modified system were limited to < 4% under even extreme temperature conditions.

The buoy samplers were modified bulk collectors deployed on oceanographic buoys as indicated above except three, polyethylene funnels draining into three-10 l polyethylene containers were used instead of the standpipe and liner. Rainfall entered the collection containers located in wooden, waterproof containers through PVC tubing. Two funnels were equipped with bug/debris screens (0.5 mm Nyltex Nylon) and one was left open for comparison.

The wet-only precipitation samplers were of the AEC design and constructed from blueprints. The polyethylene containers were 29.5 cm in diameter and 684.9 cm² in surface area. Galloway (1976), in evaluating collectors concluded that the AEC sampler was the most reliable of seven automatic collectors tested. Gear problems limited applicability in this project.

Bulk precipitation was collected on a monthly-basis by cooperative personnel at most land stations. The data resulting from such a sampling system represents total loadings over a one month period. Although event, weekly or bi-weekly samples are preferred to increase time-resolution of loading, monthly samples were selected to 1) permit comparison of our data with recent atmospheric loading studies conducted with similar samplers and frequency on the Great Lakes and 2) to require as little attention as possible by volunteer personnel maintaining the collection systems.

Table II
PRECISION OF ANALYTICAL METHODOLOGY

COMPONENT	CONCENTRATION mg/l	STD. DEV.	SIZE
TP	0.119	0.007	10
	0.050	0.001	10
	0.019	0.006	10
TDP	0.032	<001	10
	0.011	<001	10
	0.003	<001	10
DRP	0.029	<001	10
	0.014	<001	10
	0.004	<001	10
DRSi	1.40	0.01	5
	0.68	<001	5
	0.17	0.006	5
SO ₄	10.0	0.2	10
	4.3	0.1	10
Cl	7.3	1.0	10
	3.0	0.7	10
TOC	24.5	0.4	5
	16.1	2.6	5
	6.1	0.5	5
TIC	15.2	1.2	5
	5.9	0.4	5
	2.6	0.3	5
Ca	4.32	0.08	10
Mg	0.88	0.01	10
Na	0.69	0.01	10
K	0.41	0.01	10
COND. ^a	102.2	0.3	5
	66.9	1.1	5
	31.9	0.6	5
Particulates	151.2	25.9	5
	59.4	2.8	5
	22.9	1.5	5

a μ S/cm

Precipitation samples were collected at the end of each month and mailed to the Great Lakes Research Facility (GLRF) in Milwaukee or retrieved by project personnel. All samples were collected according to the same procedure with particular emphasis on sample homogeneity and contamination problems. Visual observations of sample condition were included in sample mailing and evaluated upon receipt. Occasionally, monthly samples were not received due to mailing difficulties which sometimes limited the proper statistical evaluation of loading data. However, the large number of sampling sites in operation minimized the impact of sample loss from individual sites.

Chemical Analysis

Bulk and wet-only precipitation samples were analyzed for total (TP), total dissolved (TDP) and dissolved reactive P (DRP) using the heteropoly blue method as modified by Eisenreich *et al.*, (1975). Samples were filtered the day of receipt through washed 0.4 μ m cellulose nitrate membranes (Sartorius 113 06) which have low P blanks and analyzed within 96 hours. Dissolved reactive Si (DRSi) was determined on membrane filtered samples within 96 hours by the method described in Standard Methods (1971). Sulfate (SO_4) was determined by membrane-filtered samples by the turbidimetric method and chloride (Cl) by the mercuric nitrate procedure (Standard Methods, 1971). Ca, Mg, Na and K were determined using a Perkin Elmer 503 Atomic Absorption Spectrophotometer with (Ca, Mg) or without (Na, K) La addition. Total organic and inorganic carbon were determined on unfiltered samples preserved by freezing using a modified Beckman Infrared Carbonaceous Analyzer (Maier *et al.*, 1974). Dissolved organic and inorganic carbon were determined in a similar manner on samples filtered through pre-combusted Whatman GF/C filters. Particulates were determined by a gravimetric procedure and specific conductance measurements were made with a Leeds and Northrup electrical conductivity bridge at 25° C. A combination glass electrode was used to determine pH.

No chemical preservatives were added to collected samples in the field or laboratory to minimize biological transformations so as to limit contamination. Contamination due to polyethylene liners was negligible as determined by leaching experiments. Analytical precision typically ranged from 1 to 10% depending on parameter and concentration.

SECTION 5

RESULTS AND DISCUSSION

LOADING CALCULATION

The principal objective of this investigation was to determine the atmospheric loading of P and other chemical components to Lake Michigan. To this end, 23 land-based sites were operated for 18 months in 1975-1976 in which monthly bulk precipitation (wet and dry) was collected and analyzed. Chemical loading rates were calculated by multiplying the analytical concentration of a monthly-collected sample by the volume of precipitation and dividing by the collector surface area.

$$\text{LOADING RATE} = \frac{\text{Conc. } (\mu\text{g}/\ell) \times \text{Volume } (\ell)}{506.45 \text{ cm}^2}$$

Average monthly loading rates for each site were obtained by summing individual monthly loading rates over all months and dividing by the number of months sampled. To convert to loading rates expressed as $\text{g}/\text{m}^2/\text{yr}$, multiply the loading rate expressed as $\mu\text{g}/\text{cm}^2/\text{mo}$ by 0.12.

Annual lake-wide loading is calculated by multiplying the mean monthly loading rate (all sites) by the number of months per year, the surface area of Lake Michigan (58016 Km^2) and a unit conversion factor ($10^{-9} \mu\text{g}/\text{Kg}$):

$$\text{ANNUAL LOADING} = \text{LOADING RATE} \times 12 \times 5.80 \times 10^{14} \text{ cm}^2 \times 10^{-9} \text{ Kg}/\mu\text{g}$$

(Kg/year) ($\mu\text{g}/\text{cm}^2/\text{mo}$)

Calculation of annual loadings based on mean loading rates determined from all sites heavily biases the loading value to the southern half of the lake where municipal and industrial activity is greatest. Two modifications of the above loading approach were implemented: 1) a mean loading rate was determined for each chemical parameter expressed in $\mu\text{g}/\text{cm}^2/\text{mo}$ for northern and southern Lake Michigan separately; and 2) the mean monthly loading rates for the Milwaukee and Chicago areas were averaged to obtain a value typical of the two metropolitan areas. Collection sites used in computation of the northern Lake Michigan loading were 1, 2, 3, 4, 5, 6, 17, 18 and 21. Likewise, southern sites were (7, 9, 10), 11, (12-15), 16, 22 and 23. Site #8 was not used in the Milwaukee averages due to local source contamination. These modifications permit a better estimate of lake loading as well as an improved evaluation of atmospheric source impact due to the generally rural and forested northern half of the basin versus the urban-industrial south.

Atmospheric Loading to Lake Michigan

The efficiency of precipitation collection by the bulk collectors was evaluated by placing a bulk sampler within 10 m of a weather service collector at Milwaukee's Billy Mitchell Field. Table III lists the precipitation collected in the two collectors for 1976 on a month by month basis. The bulk sampler collected $86 \pm 5\%$ of the rain gage precipitation from January through December. The constant percentage throughout 1976 encompassing rain and snow months suggests differences noted were due to differences in samplers rather than sample loss, and that the bulk collector estimated adequately precipitation falling in either form.

Figure II shows the amount of precipitation collected in 1976 and the historical mean annual precipitation amounts for nearby meteorological stations at all sampling sites. The data clearly indicate that 1976 was a dry year compared to historical precipitation records in which only 59% and 70% of the mean annual rainfall was observed in the north and south basins of Lake Michigan, respectively. Local variability in rainfall amounts did not permit comparison of weather service and bulk collector data for individual sites in 1976. The near-drought conditions experienced in the upper Lake Michigan basin suggest that dustfall inputs from the atmosphere may be significantly greater than rainfall inputs.

Bulk precipitation was collected from July, 1975 through December, 1976 but only 1976 data were used in calculating atmospheric loading rates. Figure III shows the 1976 mean monthly loading rates given in ($\mu\text{g}/\text{cm}^2/\text{mo}$) for 1976 at each land-based sampling station for TP and TDP. The observed loading rates for TP indicate a definite north-south gradation as the mean TP loading rates were 0.184 and 0.303 $\mu\text{g}/\text{cm}^2/\text{mo}$ for north and south basins of the lake, respectively. For comparison, whole-lake loading rate for TP with no differentiation of north-south inputs was 0.231 $\mu\text{g}/\text{cm}^2/\text{mo}$. Increased loading rates were also observed for the eastern shore of Lake Michigan versus the western side. This behavior likely signifies differences in soil types whereas north-south variations were due to urban-industrial activity.

A compilation of mean loading rates for TP derived from the literature converted to units of $\mu\text{g}/\text{cm}^2/\text{mo}$ is given in Table IV. Values range from 0.074 to 0.850 $\mu\text{g}/\text{cm}^2/\text{mo}$. The TP loading rate determined for the northern Lake Michigan basin in this study (0.184 $\mu\text{g}/\text{cm}^2/\text{mo}$) compares favorably with the value reported for the Upper Great Lakes (0.140 $\mu\text{g}/\text{cm}^2/\text{mo}$) and Lake Michigan (0.144 $\mu\text{g}/\text{cm}^2/\text{mo}$) determined from wet deposition only. In comparison, the less populated and developed Lake Superior basin exhibited a loading rate of only 0.081 $\mu\text{g}/\text{cm}^2/\text{mo}$ reflecting the relative lack of urban-industrial activity. The large TP loading rates reported by Allen *et al.*, (1968), Gore (1968), Pearson and Fisher (1971) and Kluesner (1972) reflect urban and agricultural activities. Brezonik and Hendry (1977) have reported recently a TP loading rate of 4.50 $\mu\text{g}/\text{cm}^2/\text{mo}$ for north central Florida corresponding to intense atmospheric loading from phosphate mining and an annual rainfall of 145 cm.

The loading rate for TDP averaged $0.041 \pm .014$ $\mu\text{g}/\text{cm}^2/\text{mo}$ in the northern

TABLE III
COMPARISON OF PRECIPITATION COLLECTION

Month 1976	Amount		U.S.W.S. ^a	%
	Bulk Collector	cm		
Jan	2.35		2.95	80
Feb	6.32		6.73	94
Mar	15.64		17.60	89
Apr	11.25		12.73	88
May	8.08		9.58	84
June	4.96		5.77	86
July ^b				
Aug ^b	9.08		10.60	86
Sept	3.71		4.32	86
Oct	5.92		7.16	83
Nov	1.30		1.65	79
Dec	0.69		0.74	93
			Aug:	86 ± 5%

^a U.S. Weather Service gage was located 10 m from bulk collector at Milwaukee's Billy Mitchel Field.

^b Rainfall volumes are for July and August.



Figure 2. Comparison of 1976 and historical precipitation amounts at atmospheric sampling sites near Lake Michigan.



Figure 3. Atmospheric loading rates of total and total dissolved phosphorus at precipitation sampling sites near Lake Michigan - 1976.

lake basin and $0.061 + .046 \mu\text{g}/\text{cm}^2/\text{mo}$ in the south, corresponding to 22 and 20% of the TP values in the north and south, respectively. The low percentage of dissolved compared to total P may be due to conversion of dissolved to particulate forms in biotic or abiotic reactions upon standing in the field. DRP represented less than 5% of TP in nearly all cases. As a result of sampling on a monthly basis and collecting wet and dry deposition, P speciation was not feasible. Collection of wet-only precipitation on an event basis combined with rapid analysis should give best estimates of P forms in rainfall.

The annual loading of TP to Lake Michigan by the atmospheric route has been estimated by Murphy and Doskey (1976) to be 1.0×10^6 Kg P/year based on 6 collection sites and analyzing event, wet-only precipitation. The approach taken was to determine a weighted-average TP concentration in rainfall for the entire lake and multiply by the mean annual precipitation in the Lake Michigan basin (74 cm) and the surface area of the lake. The approach taken in this study was to employ a larger number of sampling sites, determine mean monthly loading rates for the north and south basins and calculate annual loadings based on lake surface area. This strategy minimizes errors due to variations in annual precipitation, deposition type or geographical location. The annual loading of TP to Lake Michigan was estimated as 1.69×10^6 Kg/year, of which 0.64×10^6 and 1.05×10^6 Kg/year deposited in the north and south basins, respectively. Table V shows the loading rates and volume-weighted average concentrations of TP, TOC, SiO_2 , SO_4 , Cl, Ca, Mg, Na, K and particulates for 1976 from which annual loading values were calculated as reported in Table VI. The calculated range of southern to northern inputs is 1.64 for TP and 1.39 for Mg to 3.04 for SiO_2 . The enhanced loading of all chemical parameters measured in the south verifies the often-made estimate that the urban-industrial complex of southern Lake Michigan contributes significant quantities of major and trace elements to the lake via the atmospheric route (Winchester and Nifong, 1971). Deposition of chemical elements other than P will be limited in this paper to providing source and removal mechanisms for P.

The difference between Murphy and Doskey's (1976) estimate of TP loading from the atmosphere and this study is due to differences in sampling strategy (bulk vs wet), number of sites, calculation method and year. Precipitation data verifies that 1976 was significantly more dry than the 1973-1974 period. Phosphorus loading has a significant dry-fall component (Pearson and Fisher, 1971) which would enhance loadings in dry years.

Loading Rate Comparisons

Atmospheric loading rates for TP observed in this study can be compared to loading data generated in the Upper Great Lakes Reference Study (CCIW, 1975) under the auspices of the International Joint Commission. Table VII lists the atmospheric loading rates for TP and other chemical components determined at Beaver Island, Michigan (Site #18) in the northern Lake Michigan basin for the period 1973-1975 and 1976. Bulk collectors using the central standpipe design were employed in both studies. The loading rates for all chemical parameters except sulfate for the period 1973-1975 were 21 to 60% of the 1976 values. Sulfate exhibited 157% greater loading in the earlier period. The near drought conditions in the area during 1976 may have

Table IV
ATMOSPHERIC LOADING RATES OF TOTAL PHOSPHORUS

LOCATION	LOADING RATE ($\mu\text{g}/\text{cm}^2/\text{mo}$)	REFERENCE
England	.167-667	Allen et al (1968)
Northern England (1959-1965)	.667	Gore (1968)
Northeastern U.S. ^a	.394	Pearson and Fisher (1971)
Northwest Ontario ^b	.333	Armstrong and Schindler (1971)
Central Wisconsin ^a	.850	Kluesner (1972)
Central Finger Lakes Region	.240	Likens (1972)
Upper Great Lakes ^a	.140	CCIW (1975)
Lake Erie ^a	~.40	Matheson (1974)
Lake Ontario ^a	.298	Shiomi and Kuntz (1973)
Lake Huron ^a (1973-1975)	.219	IJC (1976)
Georgian Bay ^a (1973-1975)	.074	IJC (1976)
North Channel ^a	.076	IJC (1976)
Lake Superior ^a (1973-1975)	.061	IJC (1976)
Lake Michigan ^c	.144	Murphy (1976)
Lake Michigan ^a Northern	.184	This Study (1977)
Southern (1975-1976)	.303	

^aBulk Deposition

^bSnow-Only Deposition

^cWet-Only Deposition

TABLE V
BULK PRECIPITATION CONCENTRATIONS AND ATMOSPHERIC LOADING
RATES FOR LAKE MICHIGAN

Component	Concentration ^a			Loading Rate ^c	
	North	South mg/l	Lake Michigan ^b	North $\mu\text{g}/\text{cm}^2/\text{mo}$	South
Phosphorus (Total as P)	0.050	0.064	0.01	0.184 (.038)	0.303 (.096)
Organic Carbon (Total as C)	3.8	6.2	4.9	13.9 (2.2)	30.2 (2.3)
Silica (Reactive as SiO_2)	0.146	0.356	0.51	0.56 (.47)	1.70 (.95)
Sulfate	3.2	5.6	16	12.2 (4.7)	26.7 (5.5)
Chloride	2.5	2.9	6	9.7 (3.8)	14.0 (4.8)
Calcium	2.38	4.32	32	9.0 (3.5)	20.7 (5.5)
Magnesium	0.67	0.78	10	2.78 (2.3)	3.8 (0.6)
Sodium	0.59	0.64	3	1.5 (1.1)	3.1 (1.5)
Potassium	0.23	0.41	1	0.88 (.34)	1.88 (.95)
Particulates	19.9	34.0	-	70.7 (33)	164.5 (89)
pH	5.28	5.56	8.0	---	---

^aWeighted-average concentration in bulk precipitation for north and south basin.

^bComponent mean concentrations for open Lake Michigan water; from Upchurch (1975) and Schelske and Roth (1973).

^cNumbers in parenthesis represent one standard deviation from the mean.

TABLE VI
ATMOSPHERIC LOADING ESTIMATES OF CHEMICAL COMPONENTS TO LAKE MICHIGAN

COMPONENT	NORTHERN ^a (10 ⁶ Kg/year)	SOUTHERN ^a	TOTAL	RATIO ^b
Phosphorus, Total as P	0.64	1.05	1.69	1.6
Organic Carbon (Total as C)	48.4	105.	154.	2.2
Silica (Reactive as SiO ₂)	1.98	6.01	7.99	3.0
Sulfate (as SO ₄)	42.5	92.9	135.	2.2
Chloride (as Cl)	33.7	48.8	82.5	1.5
Calcium	31.4	72.0	103.	2.3
Magnesium	9.40	13.1	22.5	1.4
Sodium	5.29	10.9	16.2	2.1
Potassium	3.06	6.54	9.60	2.1
Particulates	246.	573.	819.	2.3

^aNorthern and southern basin areas were assumed equal (29008 Km² each)

^bRatio: Southern Inputs/Northern Inputs

TABLE VII
COMPARISON OF ATMOSPHERIC LOADING
RATES AT BEAVER ISLAND, MICHIGAN

Parameter	Loading Rates		Ratio
	1973-1975 ^a _____ $\mu\text{g}/\text{cm}^2/\text{mo}$ _____	1976 ^b	
TP	0.100	0.180	0.56
TOC	-----	15.3	-----
SiO ₂	0.335	1.63	0.21
SO ₄	16.6	10.6	1.57
Cl	4.26	10.9	0.39
Ca	7.03	11.8	0.60
Mg	1.22	2.19	0.56
Na	0.304	0.88	0.35
K	0.304	0.85	0.36
Part.	18.3	43.0	0.43
pH ^c	5.95	5.14	-----

^aCCIW (1975); IJC (1976)

^bThis Study

^cWeighted-Average pH

resulted in increased short and long range transport of soil particles which were ultimately removed by sedimentation or washout. The similar loading behavior shown for TP, Ca and Mg in the two time periods indicate that atmospheric P may be associated with soil particles. However, Na and K exhibit a lower, but constant percentage loading in the two time periods suggesting a different source or atmospheric removal mechanism. Sulfate in remote areas is generally associated with biotic processes such as sulfide to sulfate conversion in wetland areas, long distance transport from urban-industrial centers or soil particles. Gas-to-particle conversion results in sub-micron sulfate aerosols while production of soil-derived sulfate is associated with large particles greater than 5 μm . The greater sulfate loading rate in 1973-75 compared to 1976 may be caused by efficient washout by rainfall in the former wet period.

The chemical loading rate data derived from bulk precipitation data shown in Table V were developed at land-based stations on the perimeter of Lake Michigan. Coastguard buoys outfitted with three sampling units were deployed in August, 1976 about 3-6 Km offshore to ascertain whether land-based loading rates were representative of in-lake loading. Table VIII lists the mean monthly loading rates for August-October, 1976 for land station and buoys in rural and urban areas. Buoy collectors outfitted with bug screens of a type different from land collectors contaminated rainfall and could not be used.

The loading rates calculated from buoy data exceeded corresponding land stations for TP only by a factor of 1.2. In general, other chemical loading rates from buoy data were approximately equal to or slightly less than land stations except for two parameters. In-lake particulate loading exceeded land loading off the urban area while in-lake TOC loading at the rural site was about 37% of the land loading. As expected, the buoy loading rates obtained off the urban area were greater than the rural site demonstrating the effect of urban-industrial centers on atmospheric loading of adjacent water bodies. The increased deposition of TP at buoy sites may be due to greater scavenging efficiency over water. Enhanced chemical loadings for in-lake buoys compared to land stations has been reported previously for Lake Huron (CCIW, 1975). This behavior suggests that land-derived atmospheric loading rates may underestimate TP inputs to Lake Michigan although caution should be observed in extrapolating only three months of in-lake precipitation data.

Estimated Present and Future Phosphorus Inputs

The phosphorus inputs from point and non-point sources have been determined for Lake Michigan and are compared to atmospheric inputs in Table IX for 1974 and 1976, and forecasted for the year 2000. The input of P in precipitation to Lake Michigan in 1974 was 1.0×10^6 Kg/year based on Murphy and Doskey's estimates (1976) and represented 11.8% of the total input. The percentage contribution of atmospheric P differed from the quoted value of 18% because source loading data prior to 1974 was used in the earlier calculation.

TABLE VIII
COMPARISON OF BUOY AND ADJACENT LAND STATION LOADING RATES^a

COMPONENT	LOADING RATES ^b			
	RURAL		URBAN	
	Land	Buoy	Land	Buoy
	$\mu\text{g}/\text{cm}^2/\text{mo}$			
TP	.12 (.07-.16)	.15 (.12-.21)	.29 (.22-.33)	.34 (.28-.44)
TOC	29. (21.-38.)	11. (6.8-15.)	30. (26-38)	30. (20.-39)
SiO ₂	.30 (.18-.42)	.34 (.18-.54)	.60 (.36-.78)	.56 (.30-.90)
SO ₄	16. (7.7-25.)	12. (8.3-16)	23. (14.-29.)	20. (17.-25.)
Cl	12. (7.8-17.)	3. (1.7-4.3)	17. (10.-24.)	14. (4.8-23.)
Ca	9.4 (6.1-13.)	9.5 (5.9-14.)	19. (12.-26.)	15. (11.-18.)
Mg	1.7 (.80-2.5)	1.0 (.54-1.9)	3.0 (2.0-3.9)	1.8 (1.4-2.2)
Na	.96 (.73-1.2)	.77 (.37-1.1)	1.5 (.28-2.8)	.88 (.67-1.1)
K	.54 (.51-.56)	.81 (.64-.91)	.63 (.28-.89)	.67 (.50-.92)
Part	58. (37.-79.)	48. (40.-55.)	319. (71.-785.)	146. (41.-244)

^aValues represent mean monthly loading rates for August-October, 1976.

^bNumbers in parenthesis represent range of monthly loading rates measured.

Assuming an annual P loading to Lake Michigan of 1.69×10^6 Kg/year, the percentage atmospheric contribution to total loading was 15.7%. With a 10% net decrease in industrial, municipal and tributary loadings, and a 13.1% decrease in erosional inputs by the year 2000 (PLUARG, 1974), the contribution

TABLE IX
ESTIMATED PHOSPHORUS INPUTS TO LAKE MICHIGAN^a

Source	1974	1976	2000
	—————10 ⁶ Kg/year—————		
Direct Industrial	<u>0.045</u>	<u>0.061</u>	<u>0.055</u>
Discharge ^b	(.5)	(.6)	(.6)
Direct Municipal	<u>1.09</u>	<u>1.07</u>	<u>0.96</u>
Discharge ^b	(13)	(10)	(9.7)
Tributary ^b	<u>4.97</u>	<u>4.23</u>	<u>4.00</u>
	(58.7)	(39.4)	(40.3)
Erosion	<u>1.35^c</u>	<u>3.7^d</u>	<u>3.2^e</u>
	(16.0)	(34.3)	(32.3)
Atmospheric	<u>1.00^f</u>	<u>1.69^g</u>	<u>1.69</u>
	(11.8)	(15.7)	(17.1)
TOTAL	8.46	10.75	9.91

^aNumbers in parenthesis represent percent of total.

^b4th Annual Great Lakes Water Quality Report (1976).

^cU.S. EPA (1974)

^dSonzogni and Monteith (1977)

^eInternational Reference Group on Great Lakes Pollution from Land Use Activities (1974); 13.1% decrease in erosional inputs by year 2000.

^fMurphy (1976)

^gThis study (1977)

of atmospheric P to the budget of Lake Michigan will be $\sim 15.7\%$ if atmospheric inputs remain constant. Similar estimates have been arrived at for the Great Lakes by Chapra (1977). The accuracy of the predicted inputs will depend heavily on the 80-90% removal of P from wastewater, reduction or elimination of P in detergents and implementation of minimal air quality standards for P. The latter action may be difficult or impossible to legislate.

Spatial and Temporal Variations in Loading Rates

The atmospheric loading of TP and other chemical components to Lake Michigan is heavily influenced by the north-south orientation of the lake and the large industrial complex in the Chicago-Gary area. Thus, 62% of the TP loading to Lake Michigan is deposited in the southern basin. The relative contribution of each chemical component to the total loading in the northern and southern basin is given in Figure IV. The percentage of southern loading of the total ranges from 58% for Mg to 75% for SiO_2 . The increased loading in the southern basin may be attributed to urban-industrial activity, agricultural practices in Iowa, Illinois and Indiana, and regional soil transport from the south and southwest (Murphy, 1974; Gatz, 1975; Nifong and Winchester, 1971).

Seasonal variations in TP loading rates from the atmosphere may be used to suggest sources and importance of rain versus snow deposition. Figure V shows the mean monthly loading rates in 1976 for atmospheric TP for the Chicago and Milwaukee metropolitan areas and Beaver Island, Michigan. The latter site was used to indicate relative background loading in the upper basin. Loading rates for Chicago exhibit erratic behavior, but reach maxima in March, July and early winter while Milwaukee shows a bimodal distribution in loading rates with maxima in May and October. The lag in spring loading peaks between Milwaukee and Chicago may be due to colder spring temperatures in the former. Beaver Island shows a small peak in March with major loading noted in July, matching Chicago. In general, loading decreases in the order Chicago > Milwaukee > Beaver Island. There is no apparent relationship between loading rate maxima and monthly precipitation volume indicating the importance of dry deposition. Observed spring-early summer maxima may be caused by seeds, pollen, insects (Kluesner, 1972) and agricultural fertilizing and tilling while winter peaks may result from urban activities, judging by the absence of a winter peak at Beaver Island. Snow cover inhibits atmospheric loading by reducing wind-blown dust levels. Seasonal variations in TP loading have been summarized previously by Brezonik (1976), but appeared too random for interpretation. Kramer (1976) has also observed that TP loading shows a seasonal variation increasing in spring and summer.

Figure VI summarizes the seasonal variation in TP loading rates for the north and south basins of Lake Michigan. In general, loadings were dominated by spring-summer maxima with greater fluctuations in the south. Winter loadings are decreased by $\sim 50\%$ in the south as compared to summer loading rates and were minimal in the northern basin. In contrast, Figure VII shows the temporal variations in north-south loading rates for SiO_2 and Ca. Ca and SiO_2 are derived primarily from soil in remote areas or reentrained dust in urban areas, but both may also receive contributions from industrial activity in the south. Ca and SiO_2 atmospheric loading rates are relatively constant

ATMOSPHERIC LOADING ESTIMATES OF CHEMICAL COMPONENTS TO LAKE MICHIGAN

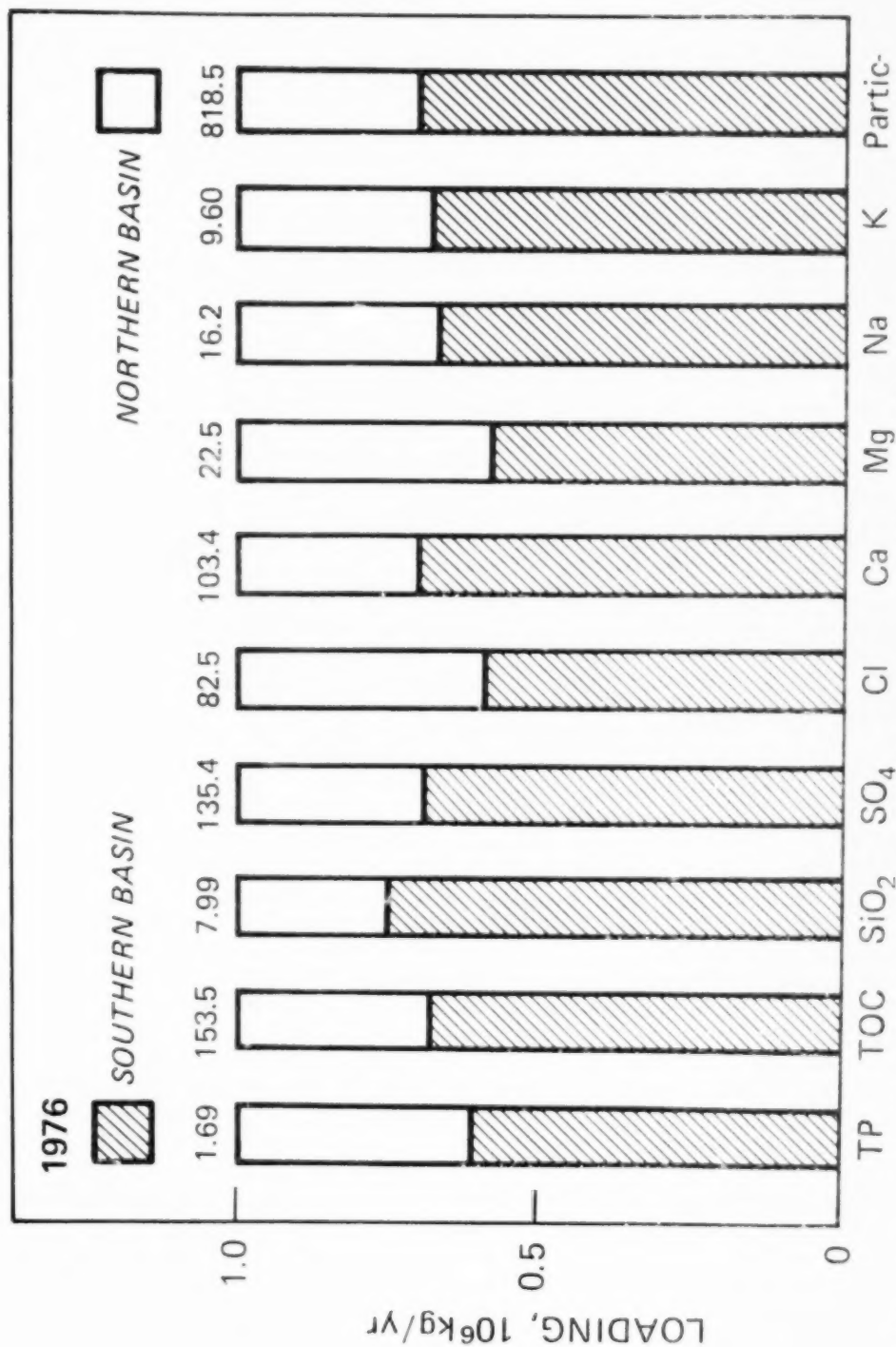


Figure 4. Atmospheric loading estimates of P, TOC, SiO_2 , SO_4 , Cl, Ca, Mg, Na, K and particulates to the southern and northern basins of Lake Michigan - 1976.

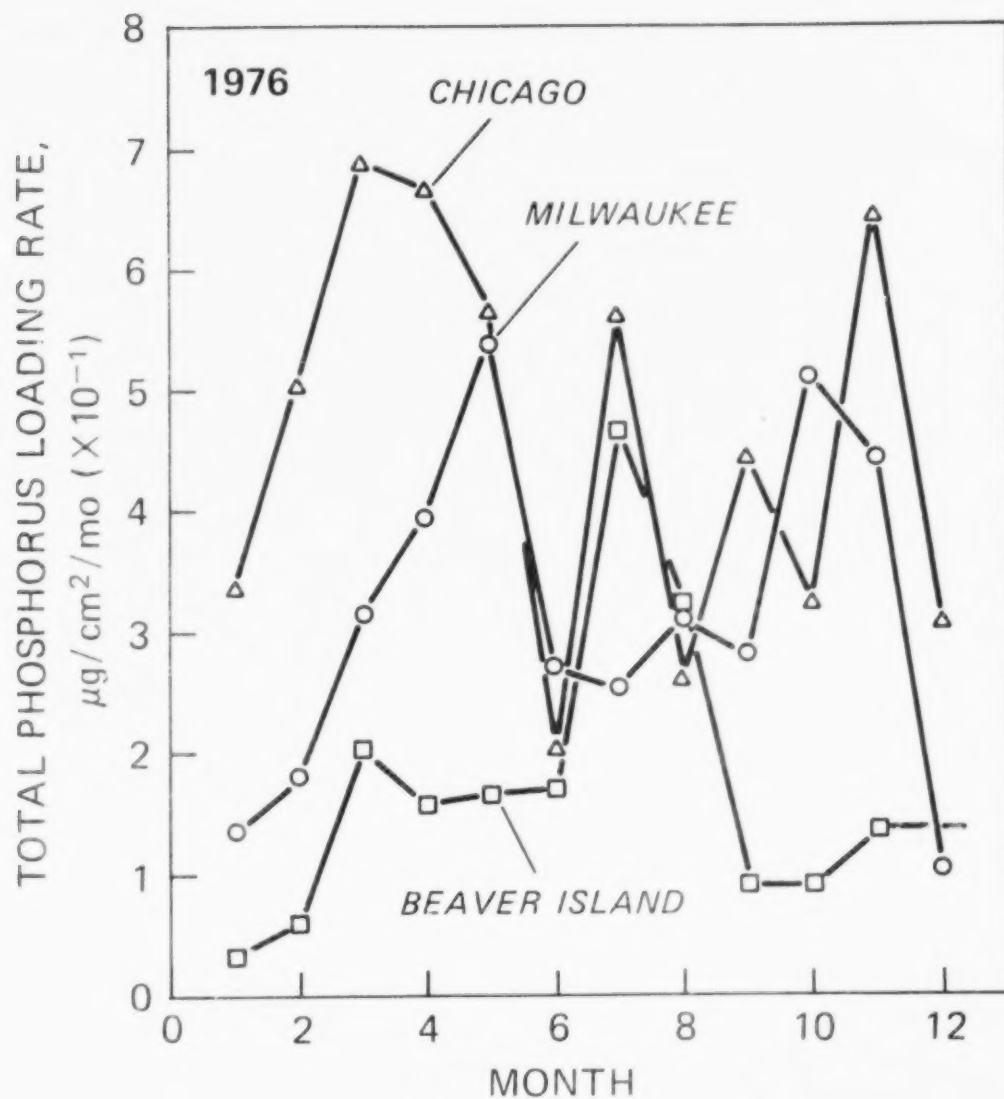


Figure 5. Seasonal variations in atmospheric loading rates measured at Beaver Island, Michigan, Milwaukee, Wisconsin and Chicago, Illinois - 1976.

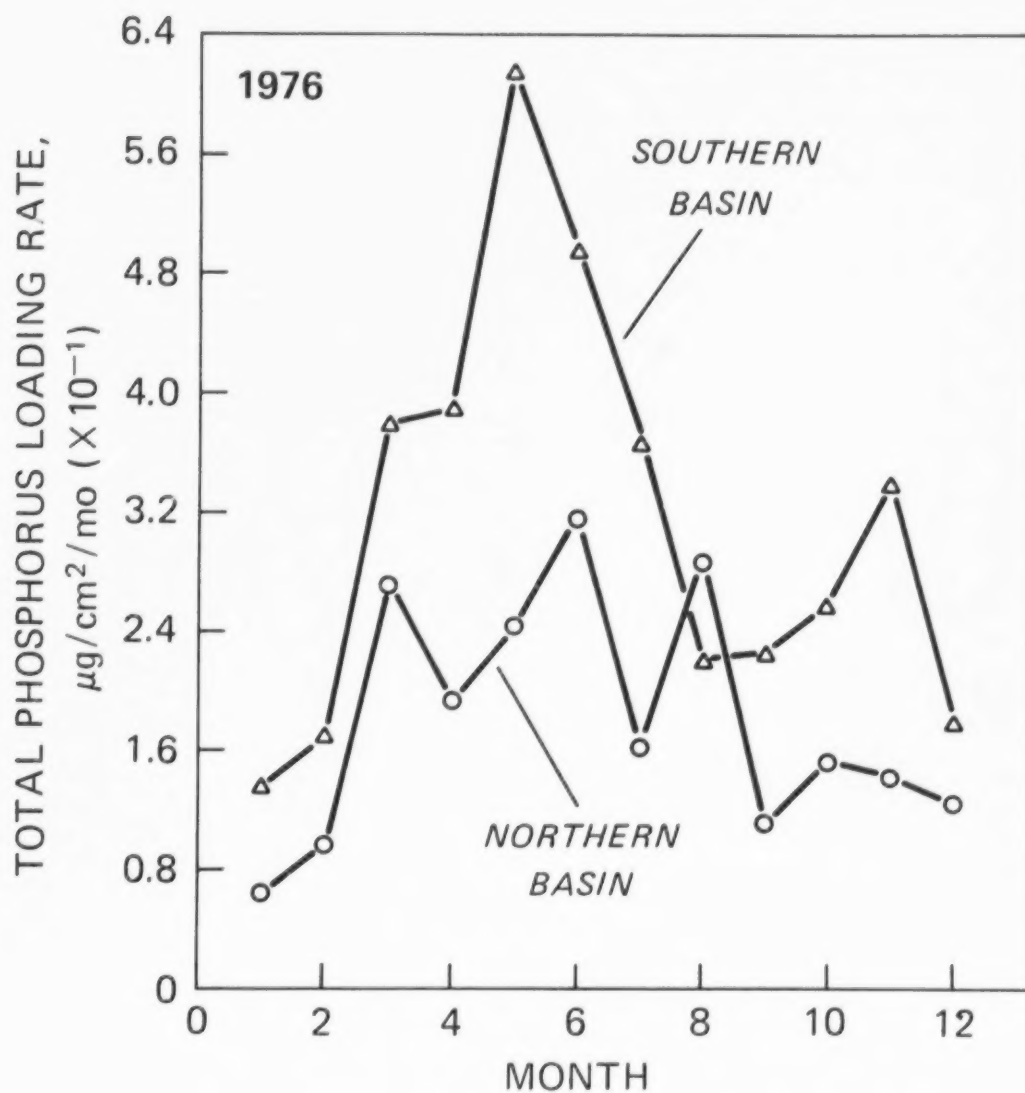


Figure 6. Seasonal variations in atmospheric loading rates to the southern and northern basins of Lake Michigan - 1976.

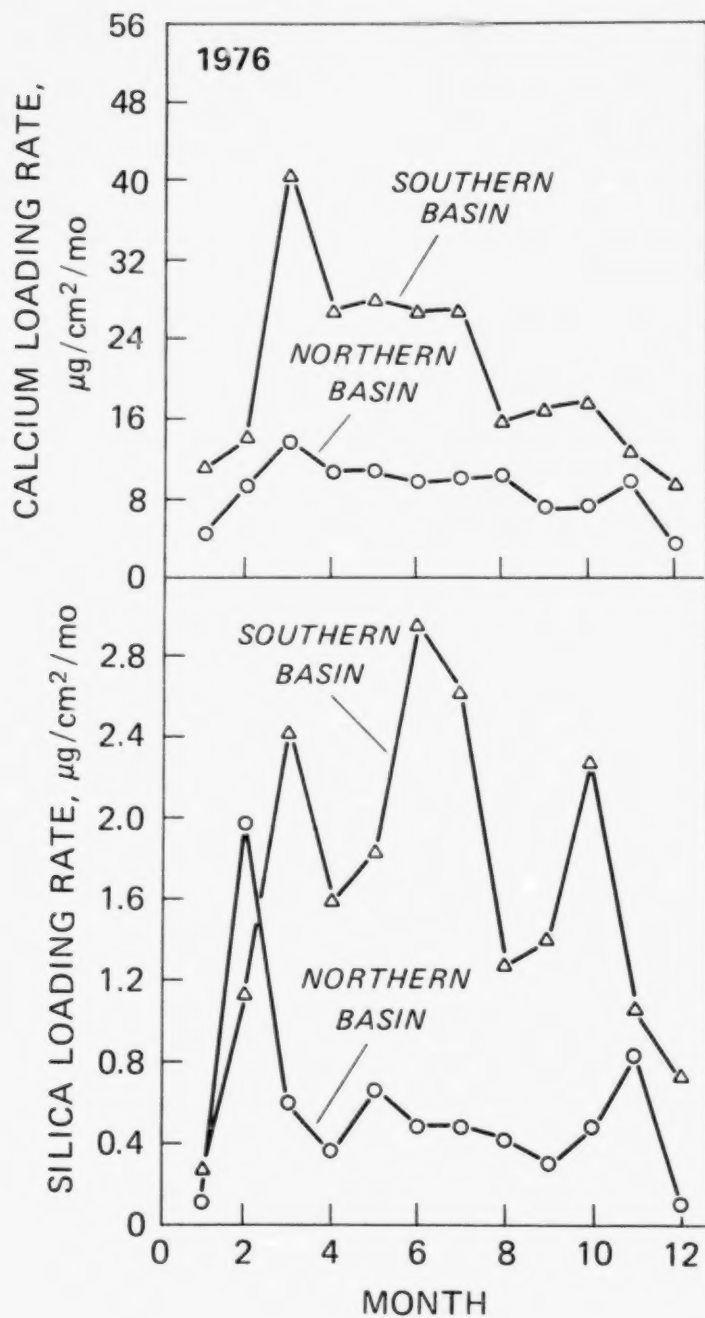


Figure 7. Seasonal variations in atmospheric loading rates of calcium and silica to the southern and northern basins of Lake Michigan - 1976.

throughout the year except for a spring maximum in the north basin while greater fluctuations occur for both in the south. Two chemical parameters more closely associated with anthropogenic sources are TOC and SO_4 . The observation is made from Figure VIII that TOC and SO_4 exhibit parallel loading behavior in the north and south basins of Lake Michigan. One explanation for the observed variations is that TOC and SO_4 deposition result from regional transport processes and have similar sources or removal mechanisms. Both TOC and SO_4 , if derived from anthropogenic sources, are associated with aerosol-size particles less than 2 μm diameter and may have long residence times in the atmosphere.

If the assumption is made that the difference in chemical loading rates for TP, Ca and SiO_2 between the north and south basins on the average is due to anthropogenic sources, then the contribution of man's activities to their loading rates may be estimated as: TP > 40%; Ca > 50%; SiO_2 > 70%; SO_4 > 40%; TOC > 60%. These values represent gross estimates based on summer loading rates and should be interpreted with caution.

Precipitation Composition Relationships

The chemical substances comprising bulk precipitation originate from two atmospheric sources: dust particles removed by sedimentation or impaction, or soluble gases or salts which are scavenged by rainfall. Chemical components originating from the two atmospheric sources would behave differently with respect to loading characteristics as a function of precipitation volume. Thus, atmospheric components which deposit on water primarily by dry fallout will be independent of precipitation amount while components removed by washout or rainout will vary with precipitation amount and number of events. Figure IX depicts the relationship between TP and Ca loading rates and annual precipitation amount. Each data point represents the mean monthly loading rate for one sampling station considered for 1976. The drawn lines represent the linear regression fit for northern sampling sites only. The southern basin data points were not considered in the calculation, but increased loadings were noted in urban-industrial areas for large precipitation volumes.

Phosphorus loading in the northern Lake Michigan basin appears independent of precipitation in agreement with the limited results of Pearson and Fisher (1971). The TP loading rate averaged $0.184 \pm .04 \mu\text{g}/\text{cm}^2/\text{mo}$. Southern basin precipitation sites showed significant data scatter and could not be interpreted readily. TP loading thus may have a large dry fallout component.

Ca loadings are dependent on precipitation volume and range from $\sim 6 \mu\text{g}/\text{cm}^2/\text{mo}$ at 30 cm to $\sim 12 \mu\text{g}/\text{cm}^2/\text{mo}$ at 60 cm. Sumi et al., (1959) identified gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in urban precipitation and attributed consistently high Ca levels to its dissolution. The precipitation dependency of Ca is inconsistent with the hypothesis that soil or dust is its major source to the atmosphere. Pearson and Fisher (1971) reported that Ca loading in bulk precipitation in the northeastern U.S. was independent of precipitation amount.

Figure X portrays similar loading-precipitation relationships for SiO_2 , SO_4 and TOC. Sulfate in precipitation originates primarily from

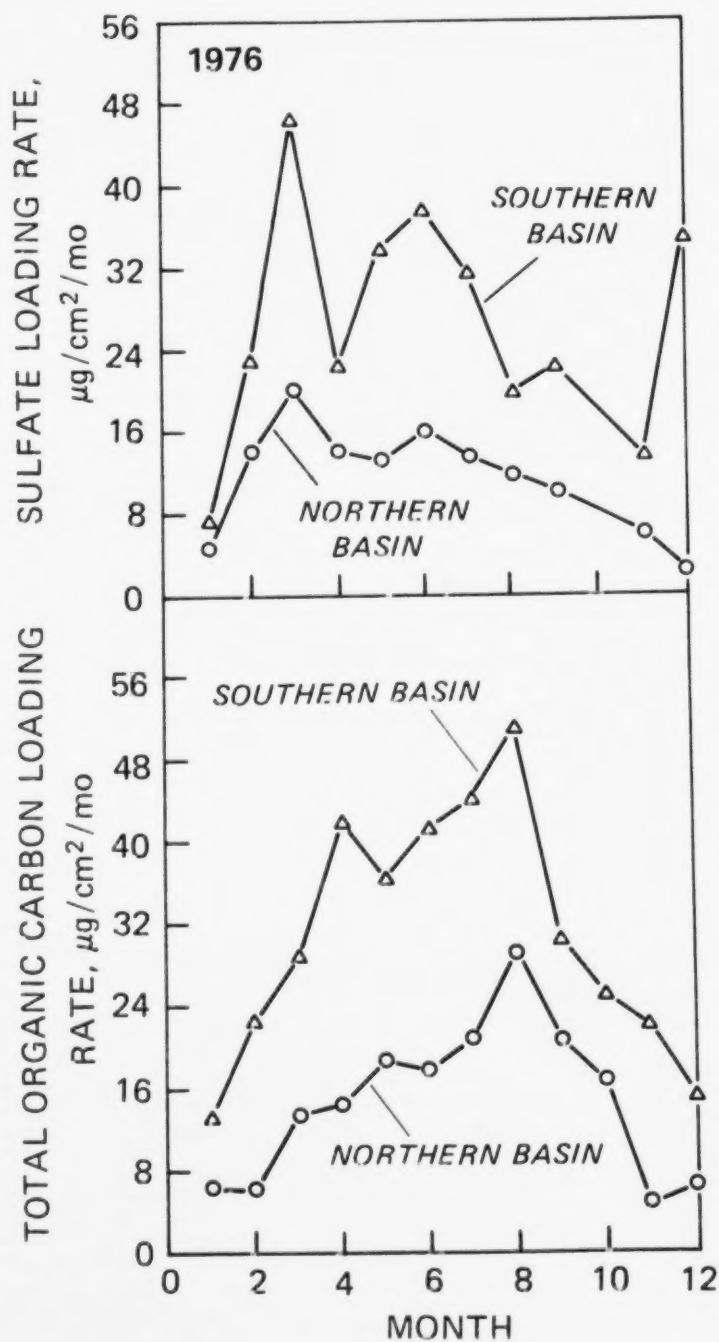


Figure 8. Seasonal variations in atmospheric loading rates of sulfate and organic carbon to the southern and northern basins of Lake Michigan - 1976.

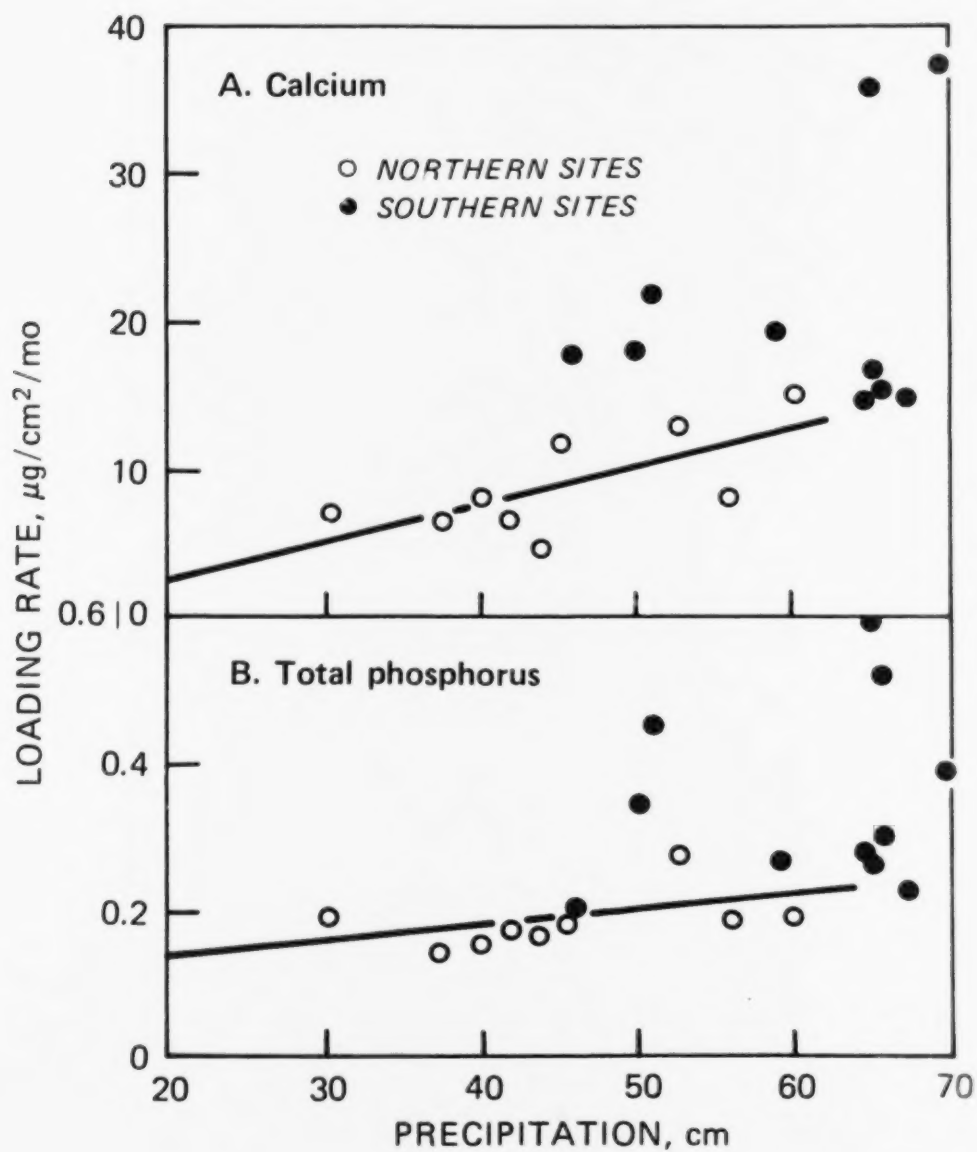


Figure 9. Relationship of atmospheric total phosphorus and calcium loading rates to precipitation amount in Lake Michigan - 1976.

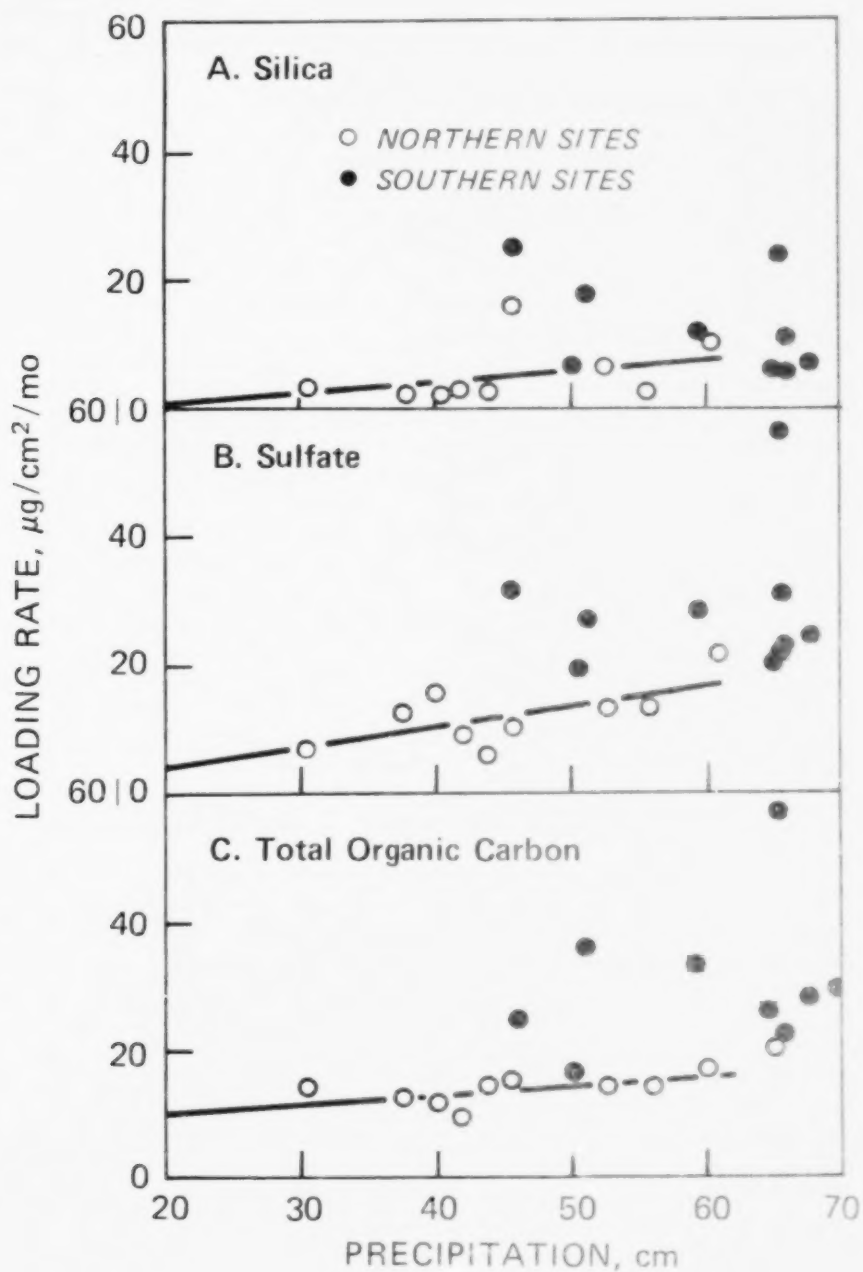


Figure 10. Relationship of atmospheric silica, sulfate and organic carbon loading rates to precipitation amount in Lake Michigan - 1976.

solution of aerosol sulfate ($<2\mu\text{m}$) and gaseous H_2S (wetlands) and SO_2 (fossil fuel combustion). The physical state of both forms suggests rainout as a major removal mechanism which is supported by its dependency on precipitation.

Andren (personal communication, University of Wisconsin, 1977) has found that a large fraction of the atmospheric organic carbon collected over Lake Michigan occurred in aerosol-size particles. The small particle size suggests that atmospheric residence times may be long. The dependency of TOC loading on precipitation amount shown in Figure X supports the hypothesis that aerosol particles are removed by washout. SiO_2 loading appears to be independent of precipitation amount, but some scatter exists limiting interpretation. SiO_2 may be derived from soil particles or power plant facilities in the form of fly ash.

Further information on sources of atmospheric P may be derived by comparing paired-element loading rates. If the principal source of Ca and Mg to the atmosphere is soil or re-entrained dust, then elements also derived from soil ought to be closely correlated. Figure XI shows the relationship of TP loading rate to that of Ca and Mg in units of $\mu\text{g}/\text{cm}^2/\text{mo}$. Each data point is the mean monthly loading rate average over all months of 1976. The strong relationship between TP and Ca, Mg loading as judged by the high correlation coefficient of the linear regression plots implies that all have a common source and/or removal mechanism. In addition, the near-zero, y-intercept of the TP-Mg plot suggests that other sources are quantitatively unimportant. The non-zero, y-intercept of the TP-Ca plot can be explained by a depletion of Ca relative to P in precipitation. Possible explanations include formation of particulate Ca (i.e., CaCO_3) on standing which would be removed by filtration prior to measurement, or to scatter in data resulting from comparison of urban and rural areas. However, soil and re-entrained dust are significant sources of atmospheric P in the Lake Michigan Basin.

Alternate techniques of source determination include comparison of elemental ratios and source enrichment factors, and determination of elemental mass balances. Calculation of P/Ca ratios in bulk precipitation yielded values ranging from 0.011 to 0.035 compared to the crustal value of 0.032 (Poldervaart, 1955). Soil would be depleted in Ca due to natural weathering increasing the P/Ca ratio. However, the average P/Ca ratio for all sites of 0.018 was similar to the ratio determined for bulk precipitation in the Upper Great Lakes (CCIW, 1976). Further evaluation of these techniques was abandoned until better soil tracers such as Al are determined. Data thus far presented suggests that wind-blown soil or re-entrained dust in the case of urban areas may be the principal source of P in bulk precipitation. If true, a comparison of monthly bulk and wet-only precipitation should demonstrate the importance of dry deposition. Table X lists the weighted-average concentrations of bulk and wet-only precipitation obtained with AEC samplers at an urban (Milwaukee) and rural (Kewaunee) site. Loading rates are not reported for wet-only samplers because collection efficiency decreased to $\sim 25\%$ of the bulk collector in winter months.

At both the rural and urban sites, TP in bulk precipitation exceeded wet-only concentrations by 600 to 700%, with higher TP concentrations observed at the Milwaukee site which is heavily influenced by local industry.

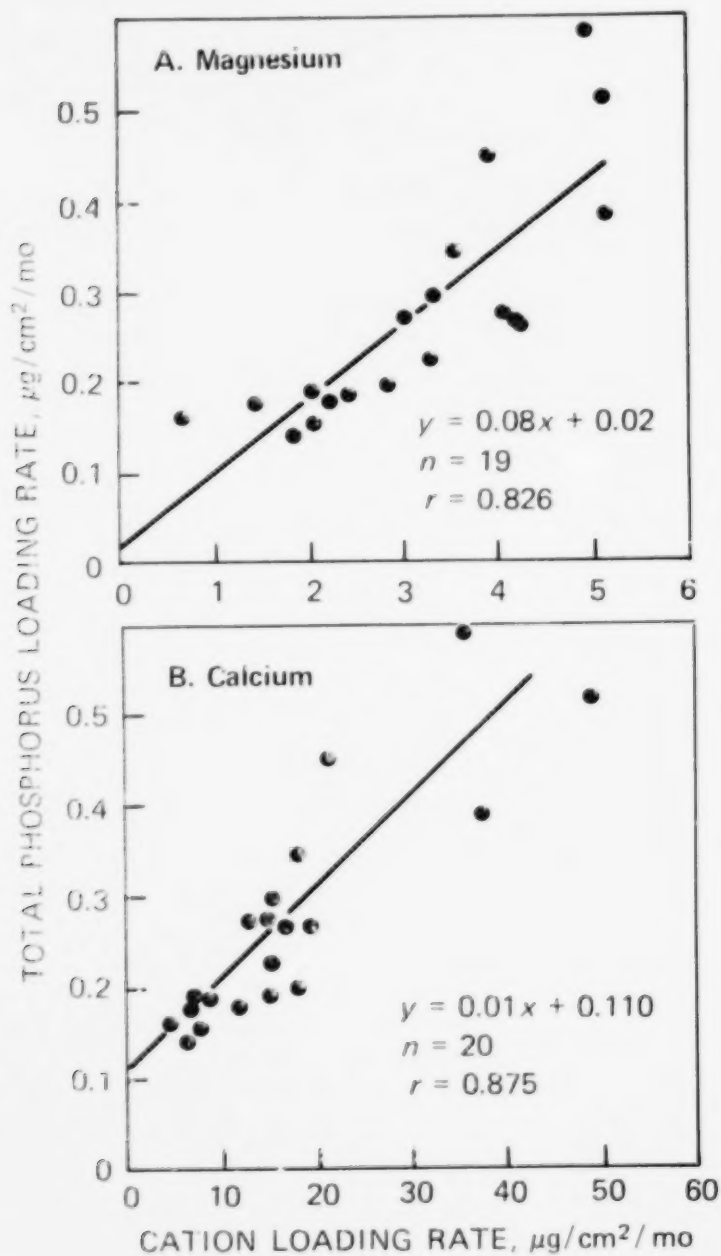


Figure 11. Relationship of atmospheric phosphorus and calcium, magnesium loading rates to Lake Michigan - 1976.

TDP and DRP concentrations at the urban site were not significantly different demonstrating the refractory nature of the particulate P derived from industrial sources (i.e., fly ash). Small, but measurable differences were observed between wet-only and bulk precipitation concentrations of dissolved P forms at the rural site suggesting that particulate P may be partially solubilized by water.

Lower pH and particulate concentrations were observed for wet-only precipitation. The free acidity noted in the wet-only samples is partially neutralized by particulate matter.

In summary, atmospheric P loading to Lake Michigan is correlated closely with Ca and Mg loading, is independent of precipitation amount in the northern basin, exhibited a large dry fallout component and is much greater in the southern than the northern basin. Wind-blown soil and re-entrained dust represent a significant source of atmospheric P addition to Lake Michigan.

Table X

COMPARISON OF BULK AND WET-ONLY PRECIPITATION^a

	MILWAUKEE (Site #8)		KEWAUNEE (Site #5)	
	<u>Wet-Only</u>	<u>Bulk</u>	<u>Wet-Only</u>	<u>Bulk</u>
	mg/l			
TP	0.031	0.190	0.008	0.057
TDP	0.007	0.009	0.003	0.010
DRP	0.002	0.003	< 0.001	0.004
PART	14.2	225.5	6.5	25.6
pH	4.36	5.34	4.48	5.96

^aWeighted-average concentrations for April-November, 1976 (#8) and May-December, 1976 (#5)

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APPENDIX A
SAMPLING STATION LOADING VALUES-1976^a

Site Number 1: Watersmeet, Michigan

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	11	9	11	11	12
Min	.039	.008	.060	2.55	.769	.119	.282
Max	.493	.210	.661	35.9	11.3	1.53	2.50
Mean	.161	.048	.273	14.4	4.72	.653	.874
Std.Dev.	.140	.054	.185	12.6	3.66	.444	.591

	K	Part.	Cl	SO ₄	pH	Vol.
Number	11	12	11	11	11	
Min	.073	5.13	ND	ND	4.30	
Max	2.73	156	11.9	15.6	5.80	
Mean	.829	48.5	7.54	6.2	4.69	43.7
Std.Dev.	.825	43.4	2.60	4.28	4.86	

^a Loading values are given in units of ug/cm²/month.

Volume represents total bulk precipitation in cm.

APPENDIX A, Contd.

Site Number 2: Stevens Point, Wisconsin

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	11	11	11	11	11
Min	.038	.009	ND	1.03	2.36	.332	.498
Max	.485	.287	.541	24.6	14.8	3.12	69.6
Mean	.176	.041	.337	9.80	6.62	1.42	7.44
Std.Dev.	.143	.078	.161	8.40	3.77	.977	20.6
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	11	11	10	9	12		
Min	.242	4.53	ND	ND	4.60		
Max	1.50	144	14.2	22.2	7.50		
Mean	.734	65.1	5.28	9.40	5.23	41.9	
Std.Dev.	.439	45.3	4.31	6.46	5.12		

Site Number 3: Green Bay, Wisconsin

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	10	10	10	9	10	10	9
Min	.055	.012	.060	4.80	1.34	.228	.474
Max	.331	.124	.841	17.0	13.9	4.33	1.70
Mean	.141	.042	.276	12.9	6.64	1.83	.888
Std.Dev.	.091	.035	.227	11.5	4.16	1.39	.454
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	10	7	7	6	10		
Min	.170	5.69	ND	ND	5.0		
Max	1.70	65.8	10.7	20.9	6.9		
Mean	.739	40.1	8.11	12.7	5.62	37.6	
Std.Dev.	.538	22.8	1.81	7.11	5.45		

APPENDIX A, Contd.

Site Number 4: Sister Bay, Wisconsin

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	9	9	8	10	9	9	9
Min	.041	.006	.060	ND	1.40	.334	.269
Max	.901	.062	1.26	42.9	12.6	5.27	1.05
Mean	.191	.028	.353	14.5	7.09	2.07	.677
Std.Dev.	.268	.017	.406	16.0	4.39	1.75	.244
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	9	8	8	7	11		
Min	.152	1.52	ND	1.68	5.0		
Max	1.23	699	11.7	11.4	6.9		
Mean	.587	126	8.25	6.92	5.62	30.4	
Std.Dev.	.349	236	3.68	3.79	5.45		

Site Number 5: Kewaunee, Wisconsin

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	10	10	10	10	9	9	8
Min	.049	.010	.060	.268	1.96	.480	.253
Max	.227	.056	.541	21.3	16.3	4.31	21.8
Mean	.155	.025	.252	12.2	8.22	2.05	3.58
Std.Dev.	.051	.014	.141	6.8	5.29	1.23	7.37
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	8	10	9	9	10		
Min	.160	10.5	ND	3.61	5.5		
Max	1.31	155	15.7	49.8	7.3		
Mean	.523	76.3	7.74	16.2	6.00	40.0	
Std.Dev.	.405	53.1	5.66	14.5	5.91		

APPENDIX A, Contd.

Site Number 6: Sheboygan, Wisconsin

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	11	11	11	11	11	11	10
Min	.052	.006	.060	3.09	1.87	.345	.379
Max	.704	.444	.661	37.5	15.5	5.37	3.36
Mean	.189	.066	.268	14.7	8.15	2.39	1.49
Std.Dev.	.183	.127	.198	10.6	4.83	1.53	1.04
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	10	10	10	11	11		
Min	.101	23.8	ND	ND	4.6		
Max	5.64	104	20.4	36.3	6.8		
Mean	1.62	62.1	10.6	13.8	5.23	55.9	
Std.Dev.	1.75	27.9	6.51	10.9	5.04		

Site Number 7: Milwaukee, Wisconsin (Linwood Ave.)

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	11	11	12	12	12	12
Min	.035	.010	.060	3.59	1.68	.259	.569
Max	.527	.171	1.26	35.5	40.9	9.21	11.8
Mean	.266	.042	.612	20.5	16.7	4.21	3.61
Std.Dev.	.148	.044	.376	9.7	11.7	3.23	3.72
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	12	12	11	8	11		
Min	.105	20.5	ND	5.23	5.0		
Max	5.18	398	19.2	34.7	7.2		
Mean	1.68	141	13.6	22.6	5.49	65.4	
Std.Dev.	1.67	113	3.37	8.99	5.39		

APPENDIX A, Contd.

Site Number 8: Milwaukee, Wisconsin (GLRF)

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	12	11	12	12	12
Min	.176	.012	.180	77.0	6.40	.418	2.51
Max	1.67	.105	2.71	862	53.4	17.3	20.4
Mean	.760	.038	1.21	327	22.4	4.74	9.49
Std.Dev.	.420	.025	.710	249	13.4	4.62	5.86
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	12	12	11	9	11		
Min	.362	279	14.7	11.2	3.7		
Max	2.62	4276	31.9	69.5	6.8		
Mean	1.26	1252	22.3	34.2	4.73	64.1	
Std.Dev.	.651	1278	6.43	16.6	4.22		

Site Number 9: Milwaukee, Wisconsin (Mitchell Field)

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	12	12	12	12	12
Min	.136	.017	.421	10.1	11.0	.352	.817
Max	.856	.255	19.5	62.6	88.2	17.5	23.4
Mean	.388	.060	4.64	29.1	37.6	5.15	7.26
Std.Dev.	.210	.067	5.18	16.0	22.6	4.96	7.26
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	12	12	11	10	11		
Min	.517	5.87	ND	12.9	6.1		
Max	4.32	938	40.0	54.7	6.9		
Mean	1.83	340	21.2	27.2	6.45	69.5	
Std.Dev.	1.04	307	11.1	12.0	6.71		

APPENDIX A, Contd.

Site Number 10: Milwaukee, Wisconsin (CHS)

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	11	12	12	12	12
Min	.058	.008	.120	8.29	3.53	.368	.210
Max	.743	.061	1.26	57.3	27.6	14.9	11.0
Mean	.276	.032	.623	26.1	14.8	4.04	3.54
Std.Dev.	.173	.018	.394	12.7	8.43	3.82	3.19
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	12	12	11	9	10		
Min	.201	28.5	ND	3.20	5.1		
Max	2.69	785	23.8	41.3	6.9		
Mean	1.10	187	16.4	20.2	5.50	64.6	
Std.Dev.	.916	213	4.32	10.5	5.55		

Site Number 11: Zion, Illinois

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	11	12	11	9	11	11	11
Min	.066	.005	.120	3.73	2.19	.169	.906
Max	.797	.068	2.34	144	41.6	11.4	13.5
Mean	.292	.031	1.19	33.7	19.5	4.18	3.03
Std.Dev.	.202	.021	.751	42.5	11.2	3.46	3.78
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	11	11	11	9	10		
Min	.107	33.9	ND	2.37	5.2		
Max	1.93	390	12.1	88.1	6.9		
Mean	.817	136	9.07	28.6	5.83	59.1	
Std.Dev.	.475	123	3.00	24.8	5.73		

APPENDIX A, Contd.

Site Number 12: Wilmette, Illinois

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	11	10	10	10	10	10	10
Min	.099	.006	ND	6.03	5.24	.744	.483
Max	.597	.469	2.22	50.3	32.5	6.88	7.41
Mean	.298	.082	1.10	22.8	15.4	3.32	2.74
Std.Dev.	.157	.138	.695	12.9	8.46	2.25	2.45
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	10	10	8	9	11		
Min	.308	15.4	ND	6.18	4.8		
Max	4.47	215	14.9	31.8	6.8		
Mean	1.84	102	12.3	21.2	5.51	65.7	
Std.Dev.	1.32	55.9	1.94	8.72	5.36		

Site Number 13: Chicago, Illinois (Shedd Aquarium)

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	11	11	11	11	11
Min	.272	.011	.240	24.4	14.4	.781	2.38
Max	.997	.436	5.35	109	150	16.2	24.2
Mean	.591	.110	2.43	57.1	39.3	4.95	7.62
Std.Dev.	.281	.155	1.53	25.7	38.7	4.77	6.73
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	11	11	10	10	11		
Min	.874	81.5	ND	18.4	5.6		
Max	5.01	1009	68.8	52.5	7.6		
Mean	2.19	287	33.2	31.1	6.19	65.3	
Std.Dev.	1.48	261	20.0	11.3	6.15		

APPENDIX A, Contd.

Site Number 14: Chicago, Illinois (DePaul Univ.)

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	12	11	12	12	12
Min	.184	.009	.240	22.5	9.98	1.10	1.94
Max	.738	.066	3.25	61.3	39.9	7.47	11.8
Mean	.452	.036	1.78	36.4	22.1	3.92	5.08
Std.Dev.	.175	.015	1.05	13.2	8.20	2.48	3.84
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	12	12	11	11	12		
Min	.685	26.2	ND	10.2	5.8		
Max	2.51	3345	36.2	42.7	7.5		
Mean	1.35	501	20.4	27.0	6.21	51.0	
Std.Dev.	.595	920	8.67	9.90	6.36		

Site Number 15: Calumet, Illinois

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	12	12	12	12	12	12	12
Min	.208	.024	1.32	27.2	24.8	1.11	1.38
Max	1.00	.083	13.5	241	69.3	11.4	12.1
Mean	.518	.051	6.55	93.9	49.3	5.12	4.58
Std.Dev.	.245	.022	4.12	70.2	16.9	3.50	3.38
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	12	12	11	11	12		
Min	.582	64.6	ND	20.3	6.1		
Max	6.92	953	38.0	105	7.8		
Mean	2.76	368	20.2	56.3	6.54	65.7	
Std.Dev.	1.79	306	9.63	25.1	6.64		

APPENDIX A, Contd.

Site Number 16: Indiana Dunes State Park

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	9	9	8	9	9	9	9
Min	.019	ND	1.14	11.4	6.68	.436	.354
Max	.566	.051	5.35	55.8	34.7	6.91	6.06
Mean	.199	.029	2.56	24.9	17.9	2.84	2.42
Std.Dev.	.176	.018	1.44	14.5	10.3	2.32	2.12
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	9	7	8	7	9		
Min	.302	35.6	5.69	10.6	5.5		
Max	22.1	200	29.1	56.6	7.4		
Mean	3.26	137	14.9	31.2	6.22	46.0	
Std.Dev.	7.11	64.9	9.39	16.6	6.00		

Site Number 17: Ludington, Michigan

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	11	11	11	11	11	11	11
Min	.092	.009	.060	4.32	5.71	.635	.825
Max	.317	.067	1.92	36.5	34.2	23.8	7.25
Mean	.190	.033	1.01	17.5	2.54	8.69	2.74
Std.Dev.	.077	.020	.622	9.30	1.77	8.65	2.09
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	11	11	10	9	11		
Min	.136	3.00	ND	ND	5.9		
Max	2.87	551	39.7	35.6	8.3		
Mean	1.18	123	17.7	21.2	6.46	60.2	
Std.Dev.	.740	153	10.2	9.58	6.35		

APPENDIX A, Contd.

Site Number 18: Beaver Island, Michigan

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	10	11	11	11	11	11	11
Min	.032	.012	.027	ND	3.68	.526	.064
Max	.466	.056	14.3	59.6	44.1	9.13	2.52
Mean	.180	.030	1.63	15.3	11.8	2.19	.875
Std.Dev.	.129	.017	4.21	16.5	11.9	2.48	.662
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	11	10	10	10	10		
Min	.217	4.54	ND	ND	4.7		
Max	2.73	141	25.9	23.1	6.8		
Mean	.851	43.0	10.9	10.6	5.14	45.4	
Std.Dev.	.788	42.0	9.06	7.15	5.08		

Site Number 21: Sleeping Bear Dunes, Michigan

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	10	10	10	10	10	10	10
Min	.055	ND	.117	ND	6.47	.691	.351
Max	1.15	.187	4.17	59.0	25.7	6.23	1.98
Mean	.274	.056	.671	14.2	12.9	3.01	1.12
Std.Dev.	.359	.058	1.24	17.0	5.44	1.54	.521
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	10	10	9	10	10		
Min	.050	16.3	ND	ND	5.2		
Max.	2.15	157	16.5	30.9	7.6		
Mean	.863	52.5	12.2	13.1	5.90	52.7	
Std.Dev.	.646	41.9	4.19	7.45	5.71		

APPENDIX A, Contd.

Site Number 22: Grand Haven, Michigan

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	11	11	11	12	12	12	12
Min	.055	.009	.110	ND	5.48	1.17	.355
Max	1.51	1.24	1.23	36.2	31.4	9.96	3.63
Mean	.346	.149	.733	16.7	18.0	3.53	1.70
Std.Dev.	.433	.362	.369	11.3	8.86	2.83	.987
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	12	12	11	10	12		
Min	.355	2.29	ND	5.04	4.7		
Max	18.1	357	18.8	42.3	7.1		
Mean	2.60	83.9	10.3	19.3	5.50	50.2	
Std.Dev.	4.97	97.9	5.50	13.0	5.16		

Site Number 23: St. Joseph, Michigan

	TP	TDP	SiO ₂	TOC	Ca	Mg	Na
Number	11	11	11	11	11	11	11
Min	.023	ND	.247	ND	3.74	.647	.174
Max	.781	.092	1.73	69.1	45.9	8.48	4.22
Mean	.228	.039	.762	28.2	15.1	3.29	1.83
Std.Dev.	.212	.028	.472	23.7	11.9	2.56	1.33
	K	Part.	Cl	SO ₄	pH	Vol.	
Number	11	11	10	9	10		
Min	.178	7.48	ND	5.35	4.5		
Max	2.05	248	21.6	49.7	7.0		
Mean	1.00	92.4	10.9	24.0	5.10	67.4	
Std.Dev.	.762	74.6	5.89	14.4	4.99		